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# Cluster-size distributions for irreversible cooperative filling of lattices. I. Exact one-dimensional results for coalescing clusters

## Abstract

We consider processes where the sites of an infinite, uniform lattice are filled irreversibly and cooperatively, with the rate of adsorption at a site depending on the state of its nearest neighbors (only). The asymmetry between empty and filled sites, associated with irreversibility, leads one to consider the closed infinite coupled hierarchies of rate equations for probabilities of connected and singly, doubly, etc., disconnected empty subconfigurations and results in an empty-site-shielding property. The latter allows *exact* solutions, via truncation, of these equations in one dimension and is used here to determine probabilities of filled  $s$ -tuples,  $f_s$  ( $f_1 \equiv \theta$  is the coverage), and thus of clusters of exactly  $s$  filled sites,  $n_s \equiv f_s - 2f_{s+1} + f_{s+2}$  for  $s \leq 13$  and 11, respectively. When all rates are nonzero so that clusters can coalesce, the  $f_s$  and  $n_s$  distributions decay exponentially as  $s \rightarrow \infty$ , and we can accurately estimate the asymptotic decay rate  $\lambda(\theta) \equiv \lim_{s \rightarrow \infty} f_{s+1}/f_s = \lim_{s \rightarrow \infty} n_{s+1}/n_s$ , where  $0 = \lambda(0) \leq \lambda(\theta) \leq \lambda(1) = 1$ . Divergent behavior of the average cluster size, as  $\theta \rightarrow 1$ , is also considered. In addition, we develop a novel technique to determine *directly* the asymptotic decay rate  $\lambda(\theta)$  and indicate its extension to higher-dimensional irreversible cooperative filling (and to other dynamic processes on lattices).

## Disciplines

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## Comments

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# Cluster-size distributions for irreversible cooperative filling of lattices.

## I. Exact one-dimensional results for coalescing clusters

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We consider processes where the sites of an infinite, uniform lattice are filled irreversibly and cooperatively, with the rate of adsorption at a site depending on the state of its nearest neighbors (only). The asymmetry between empty and filled sites, associated with irreversibility, leads one to consider the closed infinite coupled hierarchies of rate equations for probabilities of connected and singly, doubly, etc., disconnected empty subconfigurations and results in an empty-site-shielding property. The latter allows *exact* solutions, via truncation, of these equations in one dimension and is used here to determine probabilities of filled  $s$ -tuples,  $f_s$  ( $f_1 \equiv \theta$  is the coverage), and thus of clusters of exactly  $s$  filled sites,  $n_s \equiv f_s - 2f_{s+1} + f_{s+2}$  for  $s \leq 13$  and 11, respectively. When all rates are nonzero so that clusters can coalesce, the  $f_s$  and  $n_s$  distributions decay exponentially as  $s \rightarrow \infty$ , and we can accurately estimate the asymptotic decay rate  $\lambda(\theta) \equiv \lim_{s \rightarrow \infty} f_{s+1}/f_s \equiv \lim_{s \rightarrow \infty} n_{s+1}/n_s$ , where  $0 = \lambda(0) \leq \lambda(\theta) \leq \lambda(1) = 1$ . Divergent behavior of the average cluster size, as  $\theta \rightarrow 1$ , is also considered. In addition, we develop a novel technique to determine *directly* the asymptotic decay rate  $\lambda(\theta)$  and indicate its extension to higher-dimensional irreversible cooperative filling (and to other dynamic processes on lattices).

## I. INTRODUCTION

Consider processes where "filling" events occur irreversibly and, in general, cooperatively at a lattice of localized sites.<sup>1</sup> These have numerous important applications to the description of (polymer analogous) reaction of small molecules at the sites along a polymer chain and related intramolecular (e.g., cyclization) reactions<sup>2,3</sup> [one-dimensional (1D) lattices], immobile chemisorption<sup>4</sup> and reaction between attached groups on surfaces<sup>5</sup> [two-dimensional (2D) lattices], and localized reactions in crystalline solids<sup>6</sup> [three-dimensional (3D) lattices]. In every case the characteristics of the "filled" cluster-size distribution are of basic interest.

The special case in which single sites fill randomly (having trivial local statistics) has been analyzed extensively within the context of the random site percolation problem.<sup>7</sup> For random dimer filling of nearest-neighbor (NN) sites on a 1D lattice (first analyzed by Flory<sup>8</sup> in the context of a polymer cyclization reaction), some information on the filled cluster-size distribution is available from combinatorial analyses and simulations.<sup>9</sup> Filling of single sites on a 1D lattice, with NN cooperative effects, is the prototypical model for cooperative polymer analogous reactions.<sup>2,3</sup> Characterization of the site-type statistics of the resulting copolymer is of primary importance; however, only limited exact results have been presented for the filled cluster-size distributions.<sup>3,10</sup> A clear indication of the need for application of 2D irreversible filling models to chemisorption comes from the observation that, in several systems, *small* islands of presumably immobile, adsorbed species are formed (rather than one large island, as dictated by energetic considerations alone).<sup>11</sup> There is also direct evidence of negligible surface diffusion rates in

these systems.<sup>4</sup> More generally, irreversible cooperative filling provides a very natural extension of percolation analysis from random to correlated distributions and, in fact, often constitutes a physically more realistic model.

Henceforth we shall concentrate on a basic class of cooperative processes where the sites of a lattice fill,  $o \rightarrow a$ , irreversibly with adsorption rates  $k_i$ , depending only on the number  $i=0,1,\dots,z$  of filled NN sites ( $z$  is the lattice coordination number). The final (stationary) state is not in equilibrium (and nontrivial if the lattice cannot fill completely) since the irreversible, immobile filling incorporates no equilibration mechanism.

Several avenues of investigation are available here. Analysis of Markov processes corresponding to the time evolution of such "infinite-particle systems" is being actively pursued using the abstract machinery of mathematical probability theory.<sup>12-14</sup> Existence of the dynamics and fundamental characteristics of the process are considered here. One immediate result, expected intuitively, is that probabilities for filled subconfigurations in the above filling process should be bounded below and above (at each time  $t$ ) by the corresponding trivial quantities for *random* filling at rates  $k_l = \min_i k_i$  and  $k_u = \max_i k_i$ , respectively. This result, and its rigorous verification via "coupling methods," was pointed out by Liggett.<sup>15</sup> To illustrate its usefulness, we note that the probability  $f_{\{s\}}$  of any set  $\{s\}$  of  $s$  filled sites satisfies  $[1 - \exp(-tk_l)]^s \leq f_{\{s\}} \leq [1 - \exp(-tk_u)]^s$ , suggesting large  $s$  exponential decay of  $f_s$ . Liggett<sup>15</sup> also notes that for 1D filling where  $k_0 \leq k_1 \leq k_2$ , if  $f_s$  refers to  $s$  consecutive filled sites, then a theorem of Harris<sup>16</sup> implies that  $f_{s+t} \geq f_s f_t$ , so  $\lambda \equiv \lim_{s \rightarrow \infty} (-\ln f_s / s)$  exists and is nonzero (when  $t > 0$ ) if  $k_0 > 0$ .

We emphasize that these irreversible filling models incorporate a complicated competition between irreversible

birth and growth of clusters (nucleation can occur at any time during the process). In the regime where  $0 < k_0 \ll k_i$ ,  $i \geq 1$ , the nucleation centers are, on average, well separated. Thus for 2D or 3D it is natural to analyze the structure of individual clusters. Mathematical probability theory has already provided some powerful techniques to demonstrate the existence of a large-size asymptotic shape for clusters in a class of stochastic (single) cluster-growth models.<sup>17-19</sup> These techniques and behavior should apply to the filling processes studied here, and we note, in particular, that when the  $k_i$ ,  $i \geq 1$ , are equal, these individual clusters have (asymptotically round) Eden structure.<sup>17</sup> This cluster structure should be contrasted with the fractal-like behavior seen in Witten-Sander,<sup>20</sup> Meakin-Witten,<sup>21</sup> etc., growth models (based on diffusive hopping and sticking mechanisms). In analysis of competitive cluster birth and growth, e.g., of the cluster-size distribution, comparison should be made with cluster-cluster aggregation models<sup>22</sup> also based on hopping and sticking mechanisms.

Our goal, here, is the exact quantitative determination of the probabilities  $f_s$  of  $s$ -tuples of consecutive filled sites in the 1D filling problem for arbitrary rates and a range of  $s$  up to the asymptotic regime. This will provide estimates of the asymptotic exponential decay rate  $\lambda$ . (More direct methods for determination of  $\lambda$  are also of interest.) For this reason an alternative approach, exploiting certain special features of irreversible filling, is adopted. We describe these processes (for 1D, 2D, or 3D) using a set of master equations with the rates  $k_i$  as input. Since we deal only with infinite, uniform lattices here, it is convenient to recast these as an infinite hierarchy of rate equations for subconfiguration probabilities. These can be written down intuitively and include *loss* terms, corresponding to filling of each empty site in the subconfiguration, and *gain* terms, corresponding to creation of the subconfiguration by filling of appropriate sites in subconfigurations with one less filled site. For each case, we must account for all allowed configurations of the influencing, neighboring sites and multiply by the appropriate rates.<sup>1</sup> Throughout,  $f[\sigma]$  will denote the probability of a subconfiguration of sites  $\sigma$ , each specified either empty  $o$  or filled  $a$ . Here we assume that the lattice is initially empty, and note that time evolution via the hierarchical equations preserves invariance of subconfiguration probabilities under all lattice space-group operations (including translation and reflection).

There are several special features of the hierarchy associated with irreversibility and the corresponding asymmetry between empty and filled sites. A closed subhierarchy can be obtained for very general (e.g., reversible) dynamical processes on lattices for probabilities of empty subconfigurations (by conservation of probability). However, for irreversible filling, there is a "minimal closed" subhierarchy involving just connected empty subconfigurations. Probabilities for disconnected empty subconfigurations couple to those with the same or shorter separation(s) and thus indirectly back to those for less disconnected and connected empty subconfigurations.<sup>1</sup> One can also show that walls of empty sites of thickness two, that separate the lattice into disconnected regions,

*shield* sites on one side from the influence of those on the other.<sup>1</sup> For a 1D lattice, these observations lead to exact solution of the hierarchy (as described below). However, in higher dimensions exact solution is only possible for random filling,  $k_i = k$  for all  $i$  (trivially), and "almost random" filling,  $k_i = k$  for  $i < z$ ,  $k_z \neq k$ .<sup>23</sup>

The 1D version of this process was first treated in the early 1960s, where it was recognized that the minimal closed hierarchy involves only  $f[o_n]$ , probabilities for empty  $n$ -tuples,  $o_n$ .<sup>24</sup> Exact solution followed from the observation that  $f[o_n] \equiv f[oo]q^{n-2}$  for  $n \geq 2$ , where  $q \equiv e^{-k_0 t}$ , which is, of course, a consequence of the shielding property of an adjacent pair of empty sites.<sup>10,25,26</sup> Platé *et al.*<sup>10</sup> were the first to describe the method of exact determination of more general quantities such as spatial correlations, probabilities  $f_s \equiv f[a_s]$  of filled  $s$ -tuples,  $a_s$  (i.e., "pair connectivities" in a percolation-model description<sup>27</sup>), and filled cluster probabilities,  $n_s \equiv f[oa_s o] \equiv f_s - 2f_{s+1} + f_{s+2}$  (i.e.,  $n_s \equiv \Delta^2 f_s$ , where  $\Delta m_s = m_{s+1} - m_s$ ). They determined  $n_s$  for  $s = 1, 2$ , and 3 only (which provided no insight into asymptotic behavior) and compared values with simulations.<sup>3,10</sup> We have recently presented a detailed quantitative analysis of the behavior of spatial correlations including their large-separation asymptotic decay.<sup>28</sup> The observed superexponential asymptotic decay is characteristic of a larger class of infinite-particle systems.<sup>14</sup>

In Sec. II, we briefly review the hierarchical structure and solution for monomer filling with NN cooperative effects on an infinite, uniform 1D lattice. Comparison is made of the exact equations solved here with corresponding approximate Smoluchowski-type equations. Such equations, which ignore cluster-cluster correlations, are often used to model coagulation processes.<sup>29</sup> Exact results for filled  $s$ -tuple,  $f_s$ , and filled cluster,  $n_s$ , size distributions for  $s \leq 13$  and 11, respectively, are presented in Sec. III (obtained from simultaneous integration of hundreds of exactly truncated coupled equations). We show that the average cluster size without site weighting can be obtained directly, but not the variance or average size with site weighting (for which results are also presented). In Sec. IV, we present a novel new approach for extracting directly from the (suitably recast) hierarchical equations, quantities of prime interest pertaining to the asymptotics of the cluster-size distribution (here, the asymptotic exponential decay rate). The extension of this powerful approach to higher-dimensional filling processes (and even to other models) is indicated. Some conclusions are drawn and extensions discussed in Sec. V. Specifically, we give some results for the more complicated 1D monomer filling process with NN blocking and second-NN cooperative effects (where domain boundaries occur, just as in many 2D chemisorption systems).

## II. HIERARCHIAL STRUCTURE AND SOLUTION FOR MONOMER FILLING OF AN INFINITE UNIFORM 1D LATTICE WITH NN COOPERATIVE EFFECTS

As indicated in the Introduction, the procedure for exact solution of this model reflects the special structure of

the hierarchy associated with irreversibility and the corresponding asymmetry of empty and filled sites. Since only empty sites shield, our truncation procedure operates directly on the closed subhierarchies for connected, singly disconnected, etc., empty subconfigurations. Such important quantities as the filled  $s$ -tuple probabilities,  $f_s$ , cannot be obtained directly, but must be reconstructed from empty subconfiguration probabilities. Except for  $f_1 \equiv f[a] \equiv 1 - f[o]$  and  $f_2 \equiv f[aa] = 1 - 2f[o] + f[oo]$ , disconnected empty subconfiguration probabilities are required. For example, using reflection symmetry, one has

$$\begin{aligned} f[aaaaa] &\equiv 1 - 5f[o] + 4f[oo] + 3f[o-o] + 2f[o--o] \\ &\quad + f[o---o] - 3f[ooo] - 4f[oo-o] \\ &\quad - f[o-o-o] - 2f[oo--o] + 2f[oooo] \\ &\quad + 2f[ooo-o] + f[oo-oo] - f[ooooo], \end{aligned}$$

where a hyphen denotes a single site of unspecified state.

Since the procedure for obtaining exact solutions via hierarchy truncation is described in detail in Refs. 3, 10, and 28, we only outline the basic ideas here. Probabilities for empty  $n$ -tuples satisfy the minimal closed subhierarchy<sup>1,18,19</sup>

$$\begin{aligned} -\frac{d}{dt}f[o] &= k_0f[ooo] + 2k_1f[aoo] + k_2f[aoa] \\ &= k_2f[o] + 2(k_1 - k_2)f[oo] \\ &\quad + (k_0 - 2k_1 + k_2)f[ooo], \end{aligned} \quad (2.1a)$$

$$\begin{aligned} -\frac{d}{dt}f[o_n] &= (n-2)k_0f[o_n] \\ &\quad + 2(k_0f[o_{n+1}] + k_1f[ao_n]) \\ &= [(n-2)k_0 + 2k_1]f[o_n] \\ &\quad + 2(k_0 - k_1)f[o_{n+1}] \text{ for } n \geq 2. \end{aligned} \quad (2.1b)$$

A closed set of equations can similarly be obtained for  $f[o_m \overset{j}{-} o_n]$ , for various  $j, m, n$  (where  $\overset{j}{-}$  denotes  $j$  separating sites of unspecified occupancy). These  $f$ 's couple through their rate equations to  $f$ 's for subconfigurations with additional empty sites adjacent to the empty clusters (i.e., to  $f$ 's in this class with separations  $j$  and  $j-1$  and thus, indirectly, to the  $f[o_n]$ ). More generally, multiply disconnected empty subconfigurations couple to  $f$ 's for subconfigurations with additional empty sites adjacent to these empty clusters (and thus, indirectly, back to less disconnected, and connected, empty subconfigurations).

The shielding property of adjacent pairs of empty sites (used to solve these hierarchies) is best expressed mathematically in terms of the conditional probabilities  $q[\sigma\bar{\sigma}'] \equiv f[\sigma + \sigma'] / f[\sigma']$  of (conditioned)  $\sigma$  given (conditioning)  $\sigma'$ . Empty (filled) conditioning sites  $\bar{o}$  ( $\bar{a}$ ) will be denoted by  $\phi$  ( $\alpha$ ) for typographic convenience. For example, if  $\phi_n$  denotes an empty  $n$ -tuple of conditioning sites, then one has that  $q[o\phi_n \overset{j}{-} \phi_m \cdots] \equiv q[o\phi\phi]$  for  $n \geq 2$ ,  $j, m, \dots \geq 0$ , and that  $q[o\phi\phi] (\equiv q, \text{ say}) \equiv e^{-k_0 t}$  which is compatible with (2.1b). Thus one obtains

$$\begin{aligned} f[o_n] &= q[o\phi_{n-1}]f[o_{n-1}] \\ &= \cdots = q^{n-2}f[oo] \text{ for } n \geq 2, \end{aligned} \quad (2.2a)$$

$$\begin{aligned} f[o_n \overset{j}{-} o_m] &= q[o\phi_{n-1} \overset{j}{-} \phi_m]f[o_{n-1} \overset{j}{-} o_m] \\ &= \cdots = q^{n-2}f[oo \overset{j}{-} o_m] \text{ for } n \geq 2 \end{aligned} \quad (2.2b)$$

(further reduction is possible if  $m > 2$ ), thus providing finite closed sets of equations for  $q$ ,  $f[oo]$ ,  $f[o]$ ,  $f[oo \overset{j}{-} oo]$ ,  $f[oo \overset{j}{-} o]$ , and  $f[o \overset{j}{-} o]$ .<sup>10,28</sup> Clearly, shielding further implies that the probability of any disconnected empty subconfiguration can be written in terms of  $q$ ,  $f[oo]$ , and probabilities of the type  $f[\sigma \overset{l}{-} o \overset{m}{-} o \cdots o \overset{r}{-} \sigma']$  where  $\sigma, \sigma' = o$  or  $oo$ .<sup>30</sup> All of these can be obtained by integrating a finite closed coupled set of equations.<sup>28</sup>

In Sec. III we present exact results for  $f_s$ , with  $s \leq 13$ , and thus for  $n_s$ , with  $s \leq 11$ . These have been obtained from the *simultaneous integration of hundreds of exactly truncated equations* for connected and disconnected empty subconfiguration probabilities of the type described above.

It should be realized that for the filling processes considered here, one can immediately write down an exact rate equation for any subconfiguration probability (though our exact truncation procedure has naturally led to emphasis on the empty subconfigurations above). For example, we have that

$$\begin{aligned} \frac{d}{dt}f_s &= \frac{d}{dt}f[a_s] \\ &= k_2 \sum_{\substack{i+j=s-1 \\ i,j \geq 1}} f[a_i o a_j] \\ &\quad + 2(k_1 f[oo a_{s-1}] + k_2 f[ao a_{s-1}]) \text{ for } s \geq 2, \end{aligned} \quad (2.3)$$

$$\begin{aligned} \frac{d}{dt}n_s &= \frac{d}{dt}f[oa_s o] \\ &= 2k_1 f[oo a_{s-1} o] + k_2 \sum_{\substack{i+j=s-1 \\ i,j \geq 1}} f[oa_i o a_j o] \\ &\quad - 2(k_1 f[oo a_s o] + k_2 f[ao a_s o]) \text{ for } s \geq 2, \end{aligned} \quad (2.4)$$

and note that the loss term in (2.4) can be rewritten using the identity

$$\begin{aligned} f[ao a_s o] &= f[oo a_s o] + f[aa o a_s o] \\ &= f[oo a_s o] + f[oo a o a_s o] + f[aa o a_s o] \\ &= \cdots = \sum_{i=1}^{\infty} f[oa_i o a_s o]. \end{aligned} \quad (2.5)$$

One naturally compares (2.4) and (2.5) with simpler Smoluchowski-type coagulation equations<sup>29</sup> which also have a *gain* term, corresponding to formation of a cluster of size  $s$  from coagulation of two smaller ones of sizes  $i$

and  $j$  where  $i+j=s$  (rather than  $s-1$  as above), and a *loss* term, corresponding to destruction of a cluster of size  $s$  by coagulation with any other cluster. However, in the Smoluchowski equations these terms appear as sums of products of appropriately sized cluster probabilities, in contrast to (2.4) and (2.5) where cluster-cluster correlations are clearly accounted for. Such correlations are, of course, incorporated in our exact solutions.

A closer correspondence with the coagulation equations is achieved if one makes the so-called  $B$  approximation<sup>10,31</sup> (assume independence of lengths of consecutive blocks of filled and empty sites), in which case  $q[\sigma\bar{a}\bar{o}\bar{o}']$  is replaced by  $q[\sigma\bar{a}\bar{o}]$ , and  $q[\sigma\bar{o}\bar{a}\bar{o}']$  by  $q[\sigma\bar{o}\bar{a}]$ . Then (2.4) becomes

$$\frac{d}{dt}n_s \simeq \frac{2f[aoa]}{(f[oa])^2} \left[ \frac{1}{2} \left[ 2k_1 n_0 n_{s-1} + k_2 \sum_{\substack{i+j=s-1 \\ i,j \geq 1}} n_i n_j \right] - \left[ k_1 n_0 + k_2 \sum_{i=1}^{\infty} n_i \right] n_s \right], \quad (2.6)$$

where we have defined  $n_0 \equiv f[oa]f[ooa]/f[aoa]$  and used (2.5) in writing the loss term. These approximate equations, with the replacement  $\sum_{i=1}^{\infty} n_i \equiv f[oa]$ , have been shown to give reasonable results for  $s=1, 2$ , and  $3$ .<sup>10</sup>

### III. DETAILED CHARACTERIZATION OF THE FILLED CLUSTER-SIZE DISTRIBUTION

In this section we present detailed results for the filled  $s$ -tuple and cluster-size distributions for 1D monomer filling with NN cooperative effects. In Fig. 1 we have displayed  $f_{s+1}/f_s$  and  $n_{s+1}/n_s$  as functions of  $s$  (for various  $\theta$ ), for the choice of rates  $k_0:k_1:k_2=1:\rho:\rho^2$ , with  $\rho=6, 2, \frac{1}{2}$ , and  $\frac{1}{6}$ . The more extreme cases  $\rho=20$  and  $\frac{1}{20}$  are shown in Fig. 2. Other choices of nonzero rates produce similar results. It is clear that, for each  $\theta$ ,  $f_{s+1}/f_s$  approaches a constant,  $\lambda(\theta)$  say, as  $s \rightarrow \infty$ , where  $\lambda(\theta)$  ranges between zero and unity. (In fact,  $f_{s+1}/f_s$  is *very nearly constant*, as a function of  $s$ , for moderate cooperativity.) Results presented below show that  $\lambda(\theta) \sim \rho\theta$ , as  $\theta \rightarrow 0$ , and that  $1-\lambda(\theta)$  is asymptotically proportional to  $1-\theta$ , as  $\theta \rightarrow 1$ . Since the  $n_s \equiv \Delta^2 f_s$  are second-order finite differences of the  $f_s$ , it follows that *also*  $n_{s+1}/n_s \rightarrow \lambda(\theta)$  as  $s \rightarrow \infty$ , but that  $n_{s+1}/n_s$  is more sensitive to low  $s$  deviations than  $f_{s+1}/f_s$  [particularly when  $\theta$ , and thus  $\lambda(\theta)$ , is close to unity]. Since, in both cases, the convergence to asymptotic behavior is quite rapid, we can give accurate quantitative estimates of  $f_s$  and  $n_s$  for a large range of  $s$ .

Noting that  $f_{s+1}/f_s \equiv q[a\alpha_s]$ , where  $\alpha_s$  denotes a filled  $s$ -tuple of conditioning sites, and suggestively denoting  $\lambda(\theta)$  by  $q[a\alpha_\infty]$ , one has

$$f_{s+1} = \lambda(\theta)^s \prod_{i=1}^s \left[ 1 + \frac{q[a\alpha_i] - q[a\alpha_\infty]}{q[a\alpha_\infty]} \right] \theta. \quad (3.1)$$

Since numerical results indicate that the series  $\sum_{i=1}^{\infty} (q[a\alpha_i] - q[a\alpha_\infty])$  is absolutely convergent (see

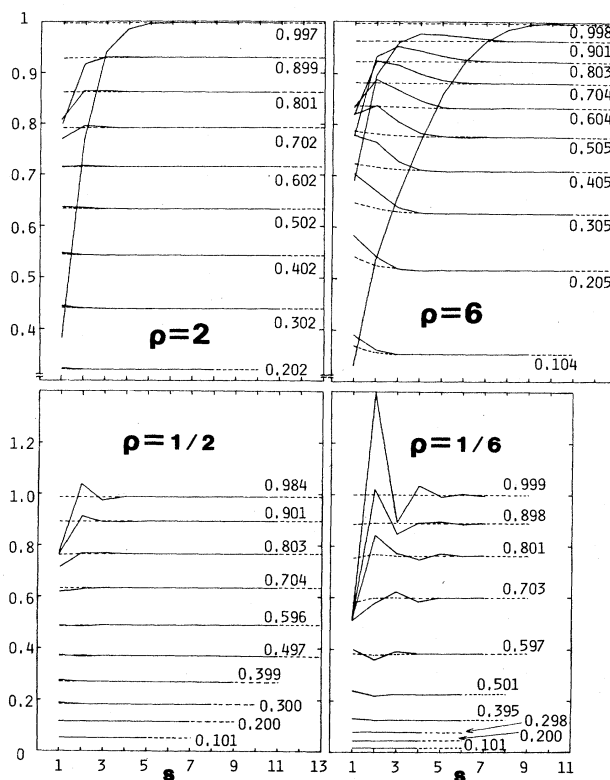


FIG. 1. Ratios  $f_{s+1}/f_s$  (---) and  $n_{s+1}/n_s$  (—) as functions of  $s$  (for various  $\theta$ , shown), for filling with NN cooperative effects with rates  $k_0:k_1:k_2=1:\rho:\rho^2$  and  $\rho=\frac{1}{6}, \frac{1}{2}, 2$ , and  $6$ .

Fig. 3), one concludes that the  $f_s$  (and thus the  $n_s$ ) exhibit asymptotic (large  $s$ ) exponential decay. Consequently, one can write

$$f_s \sim C(\theta)\lambda(\theta)^{s-1} \quad \text{and} \quad n_s \sim C(\theta)[1-\lambda(\theta)]^2 \lambda(\theta)^{s-1} \quad \text{as } s \rightarrow \infty, \quad (3.2)$$

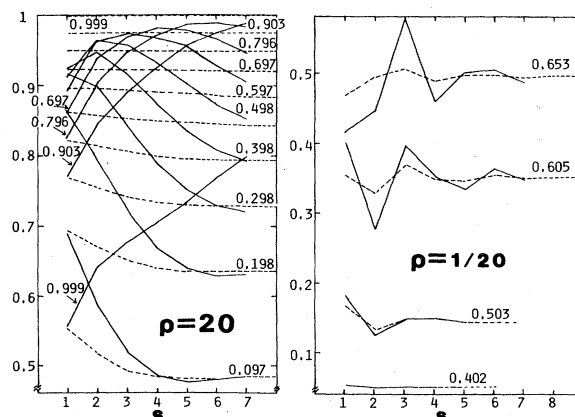


FIG. 2. Ratios  $f_{s+1}/f_s$  (---) and  $n_{s+1}/n_s$  (—) (for various  $\theta$ , shown), for filling with NN cooperative effects with  $k_0:k_1:k_2=1:\rho:\rho^2$  and  $\rho=\frac{1}{20}$  and  $20$ .

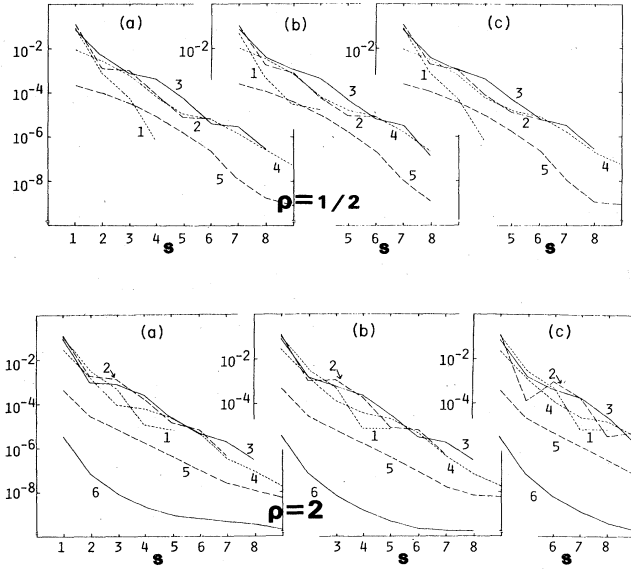


FIG. 3. Quantities (a)  $s |q[aa_s] - q[aa_\infty]|$ , (b)  $s |q[aa_s] - q[aa_{s-1}]|$ , and (c)  $s |q[aa_s] - q[aa_{s-1}]|$  as functions of  $s$  for  $k_0:k_1:k_2=1:\rho:\rho^2$  with  $\rho=1/2$  (curves 1–5 correspond to  $\theta=0.2004, 0.4971, 0.7041, 0.8999$ , and  $0.9834$ , respectively) and  $\rho=2$  (curves 1–6 correspond to  $\theta=0.2023, 0.5020, 0.7014, 0.8992, 0.9973$ , and  $0.99997$ , respectively).

where an infinite product expression for the function  $C(\theta)$  can be obtained from (3.1). We note that monotonic decrease of the  $f_s$  and  $n_s$  distributions is guaranteed by (3.2) for large  $s$ , since  $\lambda(\theta) \leq 1$ , and is only violated in the low  $\rho$  and  $s$  regime.

One nontrivial quantity, characteristic of the cluster-size distribution, which can be calculated immediately after solving the minimal closed hierarchy (2.1), is the average cluster size (without site weighting)  $n_{av}$ , given by

$$n_{av} \equiv \sum_{s=1}^{\infty} s n_s / \sum_{s=1}^{\infty} n_s. \quad (3.3)$$

Using the identity  $n_s \equiv \Delta^2 f_s$ , one can readily show that (cf. Ref. 27)

$$\sum_{s=1}^{\infty} n_s \equiv f[oa] \equiv f[o] - f[oo] \quad \text{and} \quad \sum_{s=1}^{\infty} s n_s \equiv \theta, \quad (3.4)$$

where  $f[oa] \equiv f[ao]$  gives the fraction of sites corresponding to left (or right) ends of filled clusters, i.e., the cluster density. The identities (3.3) and (3.4) are obviously valid for any site occupancy statistics.

In Fig. 4 we have displayed  $n_{av} \equiv \theta/f[oa]$ , as a function of  $\theta$ , obtained from solution of (2.1) for a choice of rates  $k_0:k_1:k_2=1:\rho:\rho^2$ , with various  $\rho$ . For  $\rho=1$ , it follows trivially from (3.3) and (3.4) that  $n_{av} \equiv (1-\theta)^{-1}$ . The  $\rho \rightarrow 0+$  limit deserves special comment. It has been recognized previously that, here, filling occurs in three stages, of sites with zero, one, and then two already filled NN, respectively, so  $(d/d\theta)f[oo]$  is piecewise constant

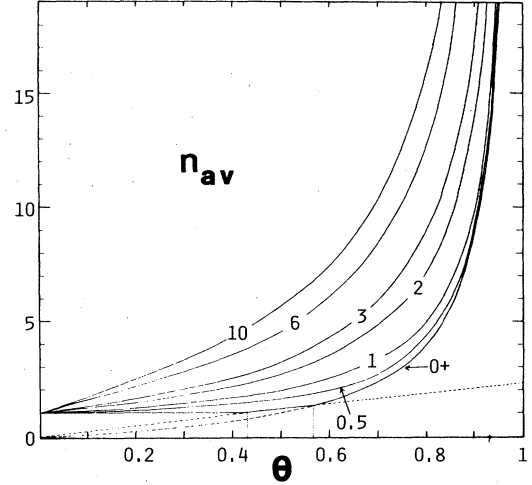


FIG. 4. Average island size (without site weighting),  $n_{av} \equiv \theta/f[oa]$ , as a function of coverage  $\theta$ , for filling with NN cooperative effects with  $k_0:k_1:k_2=1:\rho:\rho^2$  (and various  $\rho$ , shown).

with values  $-2$ ,  $-1$ , and  $0$ , since two, one, then zero empty pairs are destroyed for each site filled, respectively.<sup>1,26,32</sup> [The stages end at coverages  $(1-e^{-2})/2$ ,  $(1+e^{-2})/2$ , and  $1$ , respectively.] Thus in the first stage, one has  $f[oo] \equiv 1-2\theta$ , so  $f[oa] = \theta$  and  $n_{av} = 1$ , which is obvious since all filled sites are isolated. In the second stage where  $(d/d\theta)f[oo] = -1$ ,  $f[oa]$  is constant (obviously) with value  $\theta^* \equiv (1-e^{-2})/2$ , so  $n_{av} \equiv \theta/\theta^*$ . In the last stage one has  $f[oo] \equiv 0$ , so  $n_{av} \equiv \theta/(1-\theta)$ . It is also physically clear that  $n_{av} \rightarrow \infty$ , as  $\rho \rightarrow \infty$ , for fixed  $\theta$ , since the  $\rho \rightarrow \infty$  limit can be thought of as a single island growing (which thus has infinite size at any nonzero coverage).

Although the percolation threshold  $\theta = \theta_c$  is always trivially unity in 1D, the nature of the divergence of  $n_{av}$ , as  $\theta \rightarrow \theta_c$ , depends nontrivially on the cooperativity and is of particular interest here. Specifically, we wish to determine the critical exponent,  $\nu$ , and coefficient,  $A$ , in the relation

$$n_{av} \sim A(\theta_c - \theta)^{-\nu} \quad \text{as } \theta \rightarrow \theta_c. \quad (3.5)$$

First, note that if  $f[oo]$  goes to zero faster than  $f[o]$ , then  $f[oa] \sim f[o] \equiv 1-\theta$ , as  $\theta \rightarrow \theta_c$ , and thus we have  $A=1$  and  $\nu=1$ . This is trivially the case for random filling where  $f[oo] \equiv f^2[o]$ , so  $n_{av} \equiv (\theta_c - \theta)^{-1}$ . Furthermore, since we never have  $f[oo] \sim f[o]$ , as  $\theta \rightarrow \theta_c$ , it always follows that  $\nu=1$ .

Explicit determination of both  $A$  and  $\nu$  is easily achieved after expressing the solutions of (2.1) in terms of  $q \equiv e^{-k_0 t}$  and the reduced rates  $\rho_i = k_i/k_0$  as<sup>26</sup>

$$f[oo] = q^{2\rho_1} \exp[2(1-\rho_1)(q-1)] \quad (3.6)$$

and

$$f[o] \equiv 1 - \theta = q^{\rho_2} G(q),$$

where

$$\begin{aligned}
G(q) &= 1 + \int_1^q du \exp[2(1-\rho_1)(u-1)][2(\rho_1-\rho_2)u^{2\rho_1-\rho_2-1} + (1-2\rho_1+\rho_2)u^{2\rho_1-\rho_2}] \\
&\rightarrow G(0), \text{ a finite constant, if } 2\rho_1 > \rho_2 \\
&\sim -\rho_2 e^{2(\rho_1-1)} \ln q \quad \text{if } 2\rho_1 = \rho_2 \\
&\sim \frac{2\rho_2-2\rho_1}{\rho_2-2\rho_1} e^{2(\rho_1-1)} q^{2\rho_1-\rho_2} \quad \text{if } 2\rho_1 < \rho_2,
\end{aligned} \tag{3.7}$$

when  $q \rightarrow 0$  (i.e.,  $t \rightarrow \infty$  or  $\theta \rightarrow \theta_c = 1$ ). From these results, it follows immediately that

$$\begin{aligned}
n_{av} &\sim 1/f[oa] \sim (\theta_c - \theta)^{-1} \sim e^{k_2 t}/G(0) \\
&\text{as } \theta \rightarrow \theta_c (t \rightarrow \infty) \text{ for } 2\rho_1 > \rho_2, \tag{3.8}
\end{aligned}$$

and

$$\begin{aligned}
n_{av} &\sim 1/f[oa] \sim (\theta_c - \theta)^{-1} \sim e^{2-\rho_2} e^{k_2 t}/k_2 t \\
&\text{as } \theta \rightarrow \theta_c (t \rightarrow \infty) \text{ for } 2\rho_1 = \rho_2. \tag{3.9}
\end{aligned}$$

However, since  $f[oa] \sim [(\rho_2 - 2\rho_1)/(2\rho_2 - 2\rho_1)]f[o]$  when  $2\rho_1 < \rho_2$ , one has that

$$\begin{aligned}
n_{av} &\sim \frac{1}{f[oa]} \sim \frac{2\rho_2-2\rho_1}{\rho_2} (\theta_c - \theta)^{-1} \\
&\sim \frac{\rho_2-2\rho_1}{\rho_2} e^{2(1-\rho_1)} e^{2k_1 t} \\
&\text{as } \theta \rightarrow \theta_c (t \rightarrow \infty) \text{ for } 2\rho_1 < \rho_2. \tag{3.10}
\end{aligned}$$

Thus, in contrast to the critical exponent, for  $2\rho_1 < \rho_2$  the proportionality constant  $A$  differs from its random filling (or percolation) value of unity. The growth of the average cluster size is exponential in time, for large  $t$ , with exponent  $k_2$  for  $2\rho_1 > \rho_2$  (coalescence of clusters is the growth limiting step) and  $k_1$  for  $2\rho_1 < \rho_2$  (addition to clusters is the growth limiting step). As we shall sometimes use the choice of rates  $k_0:k_1:k_2=1:\rho:\rho^2$  ( $\rho_1=\rho_2^{1/2}=\rho$ ), we note that  $2\rho_1 \geq \rho_2$  corresponds to  $\rho \leq 2$ .

Finally, in this section we consider the behavior of the site-weighted average cluster size

$$s_{av} \equiv \sum_{s=1}^{\infty} s^2 n_s / \sum_{s=1}^{\infty} s n_s \tag{3.11}$$

and of the variance of the cluster-size distribution (without site weighting)

$$\sigma^2 \equiv \sum_{s=1}^{\infty} (s^2 - n_{av}^2) n_s / \sum_{s=1}^{\infty} n_s. \tag{3.12}$$

The main complication here is that both quantities involve the nontrivial sum

$$\sum_{s=1}^{\infty} s^2 n_s = \theta + 2 \sum_{s=1}^{\infty} f_{s+1}. \tag{3.13}$$

For numerical estimates of (3.13), it is convenient to use the identity

$$\sum_{s=1}^{\infty} f_{s+1} = [\lambda(\theta)\theta + \delta(\theta)]/[1-\lambda(\theta)], \tag{3.14}$$

where  $\delta(\theta) \equiv \sum_{s=1}^{\infty} [f_{s+1} - \lambda(\theta)f_s] = \sum_{s=1}^{\infty} f_s (q[a\alpha_s] - q[a\alpha_{\infty}])$ . It follows that  $|\delta(\theta)| \leq \sum_{s=1}^{\infty} |q[a\alpha_s] - q[a\alpha_{\infty}]|$ , which our calculations indicate is rapidly convergent (see Fig. 3). Each term approaches zero as  $\theta \rightarrow 1$ , and if we reasonably assume that  $\delta(\theta) \rightarrow 0$ , as  $\theta \rightarrow 1$ , then one has

$$s_{av} \sim \sum_{s=1}^{\infty} s^2 n_s \sim 2[1-\lambda(\theta)]^{-1} \text{ as } \theta \rightarrow \theta_c = 1. \tag{3.15}$$

In Fig. 5 we have plotted the standard deviation of the cluster-size distribution in units of the average cluster size (both without site weighting), i.e.,

$$\frac{\sigma}{n_{av}} = \left[ \sum_{s=1}^{\infty} s^2 n_s - \frac{\theta^2}{f[oa]} \right]^{1/2} \frac{(f[oa])^{1/2}}{\theta}, \tag{3.16}$$

as a function of  $\theta$ . Since it appears that  $\sigma/n_{av} \rightarrow 1$ , as  $\theta \rightarrow 1$ , we conclude from (3.16) that

$$\begin{aligned}
s_{av} &\sim \sum_{s=1}^{\infty} s^2 n_s \sim 2/f[oa] \sim 2n_{av} \sim 2A(\theta_c - \theta)^{-1} \\
&\text{as } \theta \rightarrow \theta_c = 1, \tag{3.17}
\end{aligned}$$

which, using (3.15), implies that (cf. Fig. 6 in Sec. IV)

$$1 - \lambda(\theta) \sim f[oa] \sim A^{-1}(\theta_c - \theta) \text{ as } \theta \rightarrow \theta_c = 1. \tag{3.18}$$

Finally, we note that for random filling,  $\rho=1$ , one has immediately from (3.13) and (3.14) that  $\sum_{s=1}^{\infty} s^2 n_s = \theta(1+\theta)(1-\theta)^{-1}$  and so, together with  $\sum_{s=1}^{\infty} s n_s = \theta$  and  $\sum_{s=1}^{\infty} n_s = \theta(1-\theta)$ , one concludes that  $n_{av} \equiv (1-\theta)^{-1}$ ,  $s_{av} \equiv (1+\theta)(1-\theta)^{-1}$  (see Ref. 27), and  $\sigma/n_{av} \equiv \theta^{1/2}$ .

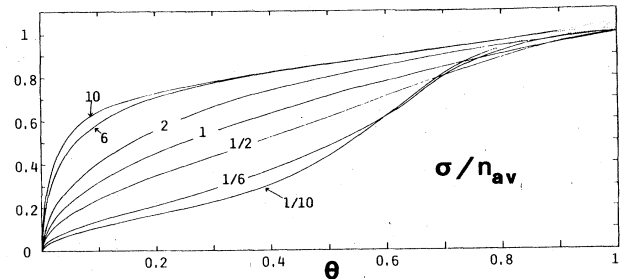


FIG. 5. Standard deviation of the cluster-size distribution in units of the average cluster size (both without site weighting),  $\sigma/n_{av}$ , as a function of  $\theta$ , for filling with NN cooperative effects with  $k_0:k_1:k_2=1:\rho:\rho^2$  (and various  $\rho$ , shown). Dotted lines, in the high- $\theta$  regime, indicate presumed spurious behavior of the numerical integration for  $\rho=6$  and  $10$  (the top line is for  $\rho=10$ ) and reasonable extrapolation for  $\rho=\frac{1}{10}$  (excessive computer time limits integration here).



#### IV. ASYMPTOTIC ANALYSIS OF THE CLUSTER-SIZE DISTRIBUTION

It is desirable to understand those structural features of the hierarchical equations which guarantee that  $f_{s+1}/f_s, n_{s+1}/n_s \rightarrow \lambda(\theta)$ , as  $s \rightarrow \infty$ , and to develop a technique for analyzing such quantities as  $\lambda(\theta)$  more directly. The strategy adopted here, which achieves these goals, involves deriving equations satisfied directly by  $\lambda(\theta)$  and related quantities, by taking appropriate limits of the (suitably recast) hierarchy equations.

Here we naturally start by considering the equation for  $q[a\alpha_s]$  conveniently expressed in the form

$$\frac{d}{dt} \ln q[a\alpha_s] = \frac{d}{dt} \ln f_{s+1} - \frac{d}{dt} \ln f_s, \quad (4.1)$$

where, after some straightforward manipulation using (2.3), one has

$$\begin{aligned} \frac{d}{dt} \ln f_{s+1} = & 2(k_1 q[o\phi\alpha_s] + k_2 q[a\phi\alpha_s])q[o\alpha_s]/q[a\alpha_s] \\ & + k_2 \sum_{\substack{i+j=s \\ i,j \geq 1}} \{(q[\alpha_i a \alpha_j])^{-1} - 1\}. \end{aligned} \quad (4.2)$$

On letting  $s \rightarrow \infty$ , one obtains for  $\lambda(\theta) \equiv \lim_{s \rightarrow \infty} q[a\alpha_s] \equiv q[a\alpha_\infty]$

$$\frac{d}{dt} \ln q[a\alpha_\infty] = k_2 \{(q[\alpha_\infty a \alpha_\infty])^{-1} - 1\}, \quad (4.3)$$

where we have assumed that various limits exist, including  $q[\alpha_\infty a \alpha_\infty] \equiv \lim_{i,j \rightarrow \infty} q[\alpha_i a \alpha_j]$ , and that, for  $i+j=s$  and  $i < j$ , one has  $q[\alpha_i a \alpha_j] - q[\alpha_i a \alpha_{j-1}] = o(1/s)$ , as  $s \rightarrow \infty$  (see Fig. 3). Calculations below support the validity of (4.3) and, thus, of these assumptions. One can check that, for random filling where  $q[a\alpha_\infty] \equiv q[\alpha_\infty a \alpha_\infty] \equiv \theta$ , (4.3) has the required solution  $\theta = 1 - e^{-k_2 t}$ . In general, one must continue to derive an equation for  $q[\alpha_\infty a \alpha_\infty]$  by considering  $\lim_{i,j \rightarrow \infty} (d/dt) \ln q[\alpha_i a \alpha_j]$ . One thus obtains (after invoking appropriate assumptions regarding existence of, and appropriate convergence to, certain limits)

$$\begin{aligned} \frac{d}{dt} \ln q[\alpha_\infty a \alpha_\infty] = & k_2 \{3(q[\alpha_\infty a \alpha_\infty])^{-1} - 5 + 2q[\alpha_\infty a \alpha_\infty]\} - 2k_1 \{(q[\alpha_\infty a - \alpha_\infty])^{-1} - 2 + q[\alpha_\infty a \alpha_\infty]\} \\ & + 2k_2 \sum_{i=1}^{\infty} \{(q[\alpha_\infty a \alpha_\infty])^{-1} - (q[\alpha_\infty a \alpha_{i-\alpha_\infty}])^{-1}\}. \end{aligned} \quad (4.4)$$

Continuing in this way, one obtains an infinite coupled set of equations for  $\lambda(\theta) \equiv q[a\alpha_\infty], q[\alpha_\infty a \alpha_\infty], q[\alpha_\infty a - \alpha_\infty], q[\alpha_\infty a \alpha_{i-\alpha_\infty}], q[\alpha_\infty a - \alpha_{i-\alpha_\infty}], \dots$

Since all these quantities clearly have zero initial conditions, it then follows that their initial time rates of change, as prescribed by the above equations, are given in indeterminate form. For example,

$$\frac{d}{dt} \ln q[a\alpha_\infty] \sim \frac{k_2}{q[\alpha_\infty a \alpha_\infty]} \left[ \text{or } \frac{d}{dt} q[a\alpha_\infty] \sim \frac{k_2 q[a\alpha_\infty]}{q[\alpha_\infty a \alpha_\infty]} \right] \text{ at } t \rightarrow 0. \quad (4.5)$$

For all other  $q$ 's where a central group of a single  $a$  site, and several  $\alpha$  and  $-$  sites, are bordered on either side by an  $\alpha_\infty$ , there are an infinite number of indeterminate terms. Most of these can be "paired" (denoted  $\nearrow$  below) as a rate  $k_i$  times a difference of reciprocals of  $q$ 's, both with  $i$   $\alpha$  sites next to the  $a$  site [cf. the last term in (4.4)]. The form of the remaining terms depends on the state of the adjacent pair of sites on either side of  $a$  and is thus completely enumerated by the following:

$$\begin{aligned} \frac{d}{dt} \ln q[\dots \alpha \alpha \alpha \alpha \dots] \sim & \frac{k_2}{q[\dots \alpha \alpha \alpha \alpha \dots]} + \frac{k_2}{q[\dots \alpha \alpha \alpha \alpha \dots]} + \frac{k_2}{q[\dots \alpha \alpha \alpha \alpha \dots]} \\ & - \frac{k_1}{q[\dots \alpha a - \alpha \alpha \dots]} - \frac{k_1}{q[\dots \alpha \alpha - a \alpha \dots]} + \nearrow, \\ \frac{d}{dt} \ln q[\dots \alpha \alpha \alpha \alpha - \dots] \sim & \frac{k_2}{q[\dots \alpha \alpha \alpha \alpha - \dots]} + \frac{k_2}{q[\dots \alpha \alpha \alpha \alpha - \dots]} + \frac{k_1}{q[\dots \alpha \alpha \alpha \alpha - \dots]} \\ & - \frac{k_1}{q[\dots \alpha a - \alpha \alpha - \dots]} - \frac{k_0}{q[\dots \alpha \alpha - a - \dots]} + \nearrow, \\ \frac{d}{dt} \ln q[\dots - \alpha \alpha \alpha - \dots] \sim & \frac{k_1}{q[\dots - a \alpha \alpha - \dots]} + \frac{k_2}{q[\dots - \alpha \alpha \alpha - \dots]} + \frac{k_1}{q[\dots - \alpha \alpha \alpha - \dots]} \\ & - \frac{k_0}{q[\dots - a - \alpha - \dots]} - \frac{k_0}{q[\dots - \alpha - a - \dots]} + \nearrow, \end{aligned} \quad (4.6)$$

$$\begin{aligned}\frac{d}{dt} \ln q[\cdots \alpha \alpha \alpha \cdots] &\sim \frac{k_2}{q[\cdots \alpha \alpha \alpha \cdots]} + \frac{k_1}{q[\cdots \alpha \alpha \alpha \cdots]} - \frac{k_1}{q[\cdots \alpha \alpha \cdots]} + \dots, \\ \frac{d}{dt} \ln q[\cdots - \alpha \alpha \cdots] &\sim \frac{k_1}{q[\cdots - \alpha \alpha \cdots]} + \frac{k_1}{q[\cdots - \alpha \alpha \cdots]} - \frac{k_0}{q[\cdots - \alpha \cdots]} + \dots, \\ \frac{d}{dt} \ln q[\cdots - \alpha \cdots] &\sim \frac{k_0}{q[\cdots - \alpha \cdots]} + \dots \text{ as } t \rightarrow 0.\end{aligned}$$

Here the dots indicate that the same configuration of  $\alpha$  and  $-$  sites, bordered by an  $\alpha_\infty$ , appears in each  $q$ .

It is clear that a choice of  $k$ 's satisfying  $q \sim kt$ , as  $t \rightarrow 0$ , consistent with (4.6), is given by

$$\begin{aligned}q[\cdots - \alpha \cdots] &\sim k_0 t, \quad q[\cdots \alpha \alpha \cdots] \sim k_2 t, \\ q[\cdots \alpha \alpha \cdots], \quad q[\cdots - \alpha \alpha \cdots] &\sim k_1 t.\end{aligned}\quad (4.7)$$

Finally, returning to (4.5), we conclude that  $q[\alpha \alpha_\infty] \sim k_1 t$  as  $t \rightarrow 0$ . This additional information allows us to consistently treat the initial indeterminacy in the  $q$  hierarchy under consideration here, thus obtaining a well-defined initial value problem. It is worth noting that these hierarchy equations are also clearly consistent with the anticipated behavior  $q[\alpha \alpha_\infty], q[\alpha_\infty \alpha \alpha_\infty], \dots \rightarrow 1$  as  $t \rightarrow \infty$ .

Exact solution of these hierarchical equations to determine, e.g.,  $\lambda(\theta) \equiv q[\alpha \alpha_\infty]$ , is not feasible because of their complicated nonlinear structure. However, to obtain approximate solutions, one could apply an  $n$ th-order Markovian approximation wherein  $q$ 's with the same conditioning configuration within  $n$  sites of  $\alpha$  are set equal (e.g., in

such an approximation  $q[\alpha \alpha_\infty], q[\alpha_\infty - \alpha \alpha_\infty], q[\alpha_\infty - \alpha \alpha_\infty], \dots$  would be set equal for  $n=2$ ). The resulting  $n=2$  estimates of  $\lambda(\theta) \equiv q[\alpha \alpha_\infty]$ , shown in Fig. 6, are quite accurate for moderate cooperativity (except near  $\theta=1$ ). We note, however, that better estimates of  $\lambda(\theta)$  can be obtained from using the exact  $q[\alpha \alpha \alpha]$ , or better,  $q[\alpha \alpha \alpha \alpha]$  (except for extremes of cooperativity and low  $\theta$ ).

This analysis is particularly significant, however, in that it provides a direct demonstration that for  $k_2 \neq 0$ ,  $\lambda(\theta) \equiv \lim_{s \rightarrow \infty} f_{s+1}/f_s$  exists as a well-behaved function of  $\theta$ , nonzero except when  $\theta=0$ . It is also clear that the origin of this behavior is the appearance of  $O(s)$  creation terms (proportional to  $k_2$ ) in the rate equation (3.4b) for  $f_s$ . (We can also conclude that if  $k_2=0$ , then  $\lim_{s \rightarrow \infty} f_{s+1}/f_s \equiv 0$  for all  $\theta$ ; this case of noncoalescing clusters is treated in detail in the following paper.<sup>33</sup>) As we shall see in Sec. V this new-found insight can be used to predict the asymptotic behavior of the filled cluster-size distribution for other more complicated 1D filling processes. Perhaps the most important aspect of this analysis is that the basic technique extends to *higher dimensions* (and even to other dynamic processes on lattices for which hierarchical rate equations apply) to provide some fundamental insights into the characteristics of the distribution of filled sites (see Appendix).

## V. DISCUSSION AND EXTENSIONS

Here we have solved the master equations (in hierarchical form) to provide the first extensive, exact analytic investigation of the filled  $s$ -tuple and filled cluster-size distributions for a 1D irreversible, cooperative filling process (specifically, monomer filling with NN cooperative effects on an infinite, uniform lattice). The solution procedure, as outlined by Platé *et al.*,<sup>10</sup> exploits shielding and coupling features of the hierarchy specific to irreversibility. Our calculations cover a sufficiently extensive range of size,  $s$ , to clearly demonstrate the transition to (large  $s$ ) asymptotic exponential decay in the above distributions (when all rates  $k_i$  are nonzero). The analytic approach allows natural investigation of the coverage or time dependence of such quantities as the average cluster size and asymptotic exponential decay rate  $\lambda(\theta)$ . Further, it facilitates a second important component of this work, specifically, development of a novel approach for extracting directly from the suitably recast hierarchical equations asymptotic properties of the cluster-size distribution such as the exponential decay rate  $\lambda(\theta)$ .

Clearly, the asymptotic exponential decay in this model is associated with the occurrence of  $O(s)$  gain terms in

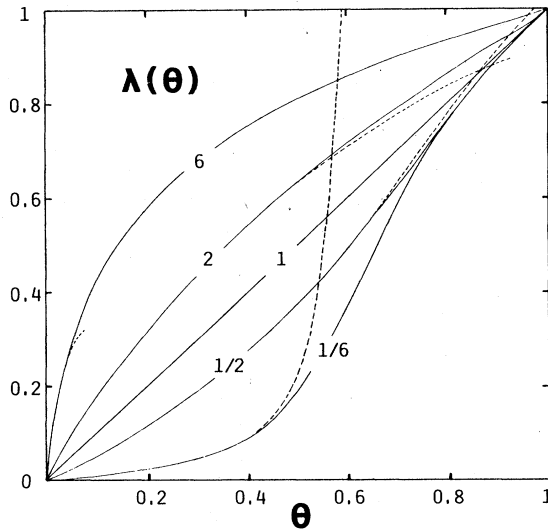


FIG. 6. Asymptotic decay rate  $\lambda(\theta) = \lim_{s \rightarrow \infty} f_{s+1}/f_s$  as a function of coverage  $\theta$ , determined from exact calculation (—) and second-order Markovian truncation (---), for filling with NN cooperative effects with  $k_0:k_1:k_2=1:\rho:\rho^2$  (and various  $\rho$ , shown). Termination of the dashed lines indicates that certain probabilities in the Markovian truncation become unphysical at these points.

the filled  $s$ -tuple,  $f_s$ , rate equation. This occurs provided  $k_2 \neq 0$  so clusters can coalesce. More generally, for any 1D irreversible filling model where "clusters" of size  $s$  can be created by filling the gap between (coalescence of) "clusters" of size  $s_1$  and  $s_2$  (where  $s_1 + s_2 = s - 1$  and  $0 \leq s_1 \leq s - 1$ ), analogous calculations suggest one still has asymptotic exponential decay of the "cluster"-size distribution. Liggett's arguments (see Introduction) support this claim as they apply to filling with arbitrary range cooperative effects and *all* rates nonzero. The following results show that it has even more general validity.

For 1D monomer filling with NN blocking and second-NN cooperative effects (so now the rates  $\hat{k}_i$  refer to the number  $i=0,1,2$  of filled second-NN), clusters of alternating empty and filled sites develop. We naturally let  $\hat{f}_s$  ( $\hat{n}_s$ ) denote the probability of the configuration  $oaoa \cdots oaoa$  or, equivalently,  $aoa \cdots oaoa$  ( $oaoa \cdots oaoa$ ) where  $s$   $a$ -filled sites appear. Here clusters can either grow together in phase (i.e.,  $\cdots oaoaooooa \cdots$ , where the center site will fill provided  $\hat{k}_2 \neq 0$ , i.e., *coalescence* can occur) or out of phase (i.e.,  $\cdots oaoaooooa \cdots$ , creating a permanent domain boundary).<sup>34</sup> Exact hierarchical solution is again possible,<sup>34,35</sup> but since an empty 4-tuple (rather than pair) of sites is required to shield, many more independent quantities exist and must be determined from exactly truncated equations (specifically,  $q = f[o_{n+1}]/f[o_n] = e^{-\hat{k}_0 t}$ ,  $n \geq 4$ ;  $f[o_i]$ ,  $1 \leq i \leq 4$ ; and  $f[o_{j_1} \cdots o_{i_1} \cdots o_{i_2} \cdots o_{j_2}]$  where  $1 \leq j_1, j_2 \leq 4$ ,  $1 \leq i_1, i_2, \dots \leq 3$ ). For  $\hat{k}_2 \neq 0$ , this model *does* fit the above criteria for asymptotic exponential decay of  $\hat{f}_s$  and  $\hat{n}_s$ . This is confirmed from the results shown in Fig. 7, obtained from a very extensive exact truncation calculation. Furthermore, if  $\hat{f}_{s+1}/\hat{f}_s \rightarrow \hat{\lambda}(\theta)$  as  $s \rightarrow \infty$ , then the analog of (4.3) becomes

$$\frac{d}{dt} \ln \hat{\lambda}(\theta) = \hat{k}_2 \{ (q[\cdots -\alpha-\alpha-a-\alpha-\alpha-\cdots])^{-1} - 1 \}. \quad (5.1)$$

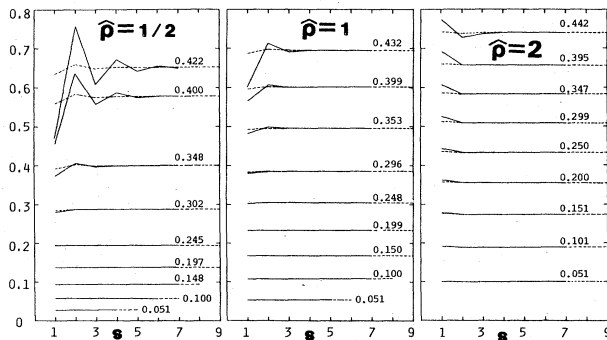


FIG. 7. Ratios  $\hat{f}_{s+1}/\hat{f}_s$  (---) and  $\hat{n}_{s+1}/\hat{n}_s$  (—) (for various  $\theta$ , shown), for filling with NN blocking and second-NN cooperative effects with rates  $\hat{k}_0:\hat{k}_1:\hat{k}_2=1:\hat{p}:\hat{p}^2$  and  $\hat{p}=\frac{1}{2}, 1$ , and  $2$ .

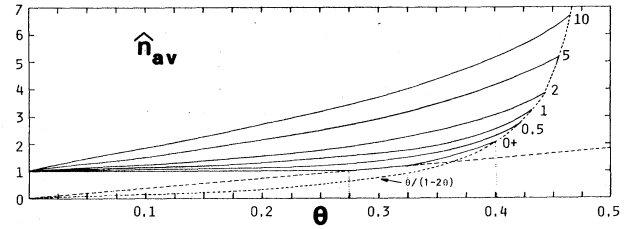


FIG. 8. Average island size (without site weighting)  $\hat{n}_{av} = \theta/f[aoa]$ , as a function of coverage, for filling with NN blocking and second-NN cooperative effects with  $\hat{k}_0:\hat{k}_1:\hat{k}_2=1:\hat{p}:\hat{p}^2$  (and various  $\hat{p}$ , shown). When  $\hat{p}=0+$ , the process occurs in three stages corresponding to filling of sites where the number of filled second-NN is zero ( $0 \leq \theta \leq \theta_1 \approx 0.2746$ ,  $\hat{n}_{av}=1$ ), one ( $\theta_1 \leq \theta \leq \theta_2 \approx 0.3243$ ,  $\hat{n}_{av}=\theta/\theta_1$ ), and two [ $\theta_2 \leq \theta \leq \theta_3 \approx 0.4011$ ,  $\hat{n}_{av}=\theta(\theta_1+\theta_2-\theta)^{-1}$ ]. Since  $f^{sat}[aoa]=f^{sat}[oo]=1-2\theta^{sat}$ , we have that  $\hat{n}_{av}^{sat}=\theta^{sat}(1-2\theta^{sat})^{-1}$ .

The behavior of the average cluster size without site weighting, straightforwardly determined<sup>34</sup> from  $\hat{n}_{av} = \theta/f[aoa]$ , with  $f[aoa] \equiv f[ao] - f[ooo]$ , is shown in Fig. 8. It is appropriate to recall the equivalence of this process to 1D dimer filling with NN cooperative effects<sup>34</sup> and note the compatibility of our results with those from earlier simulations for 1D random dimer filling.<sup>9</sup>

Finally, we note the applicability of the technique of Sec. IV to higher-dimensional irreversible filling processes (see Appendix) and anticipate that it will be useful for consideration of a variety of other dynamic processes on lattices.

Our model could be modified so that nucleation is enhanced at (or confined to) a distribution of sites specified either defective or initially filled, making it similar to those used to describe irreversible kinetic gelation<sup>36</sup> (particularly if we consider bond rather than site filling). We leave such considerations until later work, but note that we expect the long-range connectivity transition of kinetic gelation to be in a different universality class from that of the filling processes considered here.

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#### APPENDIX: IRREVERSIBLE COOPERATIVE FILLING ON A 2D SQUARE LATTICE

Consider the irreversible filling of sites on a square lattice with NN cooperative effects. Let  $k_i$ ,  $i=0,1,\dots,4$ , denote the rates for filling sites with  $i$  (already) occupied NN. Rate equations can be written down intuitively for any subconfiguration probability.<sup>1</sup> For example, using the obvious notation for subconfigurations, one obtains

$$\frac{d}{dt}f[a] = k_0 f \begin{bmatrix} o \\ o \\ o \end{bmatrix} + 4k_1 f \begin{bmatrix} o \\ a o o \\ o \end{bmatrix} + k_2 \left( 2f \begin{bmatrix} o \\ a o a \\ o \end{bmatrix} + 4f \begin{bmatrix} a \\ a o o \\ o \end{bmatrix} \right) + 4k_3 f \begin{bmatrix} a \\ a o a \\ o \end{bmatrix} + k_4 f \begin{bmatrix} a \\ a o a \\ a \end{bmatrix}, \quad (A1)$$

$$\begin{aligned} \frac{d}{dt}f[a_s] = & \sum_{\substack{i+j=s-1 \\ i,j \geq 1}} \left( k_2 f \begin{bmatrix} o \\ a_i o a_j \\ o \end{bmatrix} + 2k_3 f \begin{bmatrix} a \\ a_i o a_j \\ o \end{bmatrix} + k_4 f \begin{bmatrix} a \\ a_i o a_j \\ a \end{bmatrix} \right) \\ & + 2 \left( k_1 f \begin{bmatrix} o \\ o o a_{s-1} \\ o \end{bmatrix} + k_2 f \begin{bmatrix} o \\ a o a_{s-1} \\ o \end{bmatrix} + 2k_2 f \begin{bmatrix} a \\ o o a_{s-1} \\ o \end{bmatrix} + k_3 f \begin{bmatrix} a \\ o o a_{s-1} \\ a \end{bmatrix} + 2k_3 f \begin{bmatrix} a \\ a o a_{s-1} \\ o \end{bmatrix} + k_4 f \begin{bmatrix} a \\ a o a_{s-1} \\ a \end{bmatrix} \right), \end{aligned} \quad (A2)$$

where  $a_n$  here denotes a horizontal  $n$ -tuple of filled sites, and we have exploited various lattice group symmetries. Equation (A2) should be compared with (2.3).

If we define  $f_s \equiv f[a_s]$ , then again one can consider the behavior of  $f_{s+1}/f_s$  as  $s \rightarrow \infty$ . We naturally start by writing down the rate equation for  $q[a\alpha_s] = f_{s+1}/f_s$  and verify that its structure is compatible with the existence of a finite, nonzero (except when  $\theta=0$ ) limit  $\lambda(\theta) = \lim_{s \rightarrow \infty} q[a\alpha_s] \equiv q[a\alpha_\infty]$ , say (cf. Sec. IV). This is seen to be the case since, after taking the  $s \rightarrow \infty$  limit, one obtains

$$\begin{aligned} \frac{d}{dt} \ln q[a\alpha_\infty] = & k_2 \left( \frac{1}{q[\alpha_\infty a \alpha_\infty]} - 1 \right) - 2(k_2 - k_4) \left( \frac{q \begin{bmatrix} a \\ \alpha_\infty - \alpha_\infty \end{bmatrix}}{q[\alpha_\infty a \alpha_\infty]} - q \begin{bmatrix} a \\ \alpha_\infty \alpha_\infty \end{bmatrix} \right) \\ & + (k_2 - 2k_3 + k_4) \left( \frac{q \begin{bmatrix} a \\ \alpha_\infty - \alpha_\infty \\ a \end{bmatrix}}{q[\alpha_\infty a \alpha_\infty]} - q \begin{bmatrix} a \\ \alpha_\infty \alpha_\infty \\ a \end{bmatrix} \right), \end{aligned} \quad (A3)$$

where  $q[\alpha_\infty a \alpha_\infty] \equiv \lim_{i,j \rightarrow \infty} q[\alpha_i a \alpha_j]$ ,

$$q \begin{bmatrix} a \\ \alpha_\infty - \alpha_\infty \\ a \end{bmatrix} \equiv \lim_{i,j \rightarrow \infty} q \begin{bmatrix} a \\ \alpha_i - \alpha_j \\ a \end{bmatrix}, \dots$$

and  $q[\alpha_i a \alpha_j] \equiv f[a_{i+1+j}]/f[a_i - a_j]$ ,

$$q \begin{bmatrix} a \\ \alpha_i - \alpha_j \\ a \end{bmatrix} \equiv f \begin{bmatrix} a \\ a_i - a_j \\ a \end{bmatrix} / f[a_i - a_j], \dots$$

(assuming existence of, and appropriate convergence to, these limits). Note that one can always factor these  $q$ 's in terms of those with a single  $a$ -(filled, conditioned) site, e.g.,

$$q \begin{bmatrix} a \\ \alpha_i - \alpha_j \\ a \end{bmatrix} \equiv q \begin{bmatrix} a \\ \alpha_i - \alpha_j \\ \alpha \end{bmatrix} q \begin{bmatrix} a \\ \alpha_i - \alpha_j \end{bmatrix}$$

so

$$q \begin{bmatrix} a \\ \alpha_\infty - \alpha_\infty \\ a \end{bmatrix} \equiv q \begin{bmatrix} a \\ \alpha_\infty - \alpha_\infty \\ \alpha \end{bmatrix} q \begin{bmatrix} a \\ \alpha_\infty - \alpha_\infty \end{bmatrix}. \quad (A4)$$

Support for the proposition that the limits

$$q[\alpha_\infty a \alpha_\infty], q \begin{bmatrix} a \\ \alpha_\infty - \alpha_\infty \end{bmatrix}, \dots$$

exist and are nonzero (except when  $\theta=0$ ), which is necessary for finite, nonzero  $q[a\alpha_\infty]$  to exist, comes from writing down equations for

$$q[\alpha_i a \alpha_j], q \begin{bmatrix} a \\ \alpha_i - \alpha_j \end{bmatrix}, \dots$$

and examining the  $i, j \rightarrow \infty$  limit. The resulting equations involving new, more complex  $q$ 's with infinite numbers of filled conditioning sites and thus an infinite hierarchy are generated in this fashion. Although the existence of well-behaved solutions is difficult to prove rigorously, it seems reasonable based on the structure of these equations and particularly the capability to consistently handle the indeterminacy in the initial slopes.

The quantities describing the distribution of lengths of (horizontal) linear strings of filled sites are clearly the  $n_s = f[oa_s o] = f_s - 2f_{s+1} + f_{s+2}$ . These, of course, will only reflect the distribution of cluster linear dimensions for fairly compact contiguous clusters. Since our arguments above indicate that  $f_{s+1}/f_s \rightarrow \lambda(\theta)$  as  $s \rightarrow \infty$  (compatible with Liggett's arguments described in the Introduction<sup>15</sup>), it follows that also  $n_{s+1}/n_s \rightarrow \lambda(\theta)$  as  $s \rightarrow \infty$ .

Thus for these nontrivial 2D filling processes, which are not amenable to exact solution, we anticipate that this distribution decays like  $n_s \sim K(\theta)\lambda(\theta)^s - 1$  as  $s \rightarrow \infty$ . To obtain estimates of  $\lambda(\theta)$ , which ranges from zero to unity as  $\theta$  varies over this range, we could subject the above-

mentioned  $q$ -hierarchy equations to Markovian-type truncation approximations. Of course,  $\lambda(\theta) \equiv \theta$  for random filling, and we expect that these Markovian-type approximations will give reasonable estimates for weakly or moderately cooperative filling (cf. Sec. IV).

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